isomerize under mild conditions to cyclopentadiene. With the information presently available, it seems likely that the dehalogenation of 1,1-dibromo-2-vinylcyclopropane does not involve, as proposed,[10] intermediary formation of I and spontaneous isomerization at −78° to cyclopentadiene, the isolated product, but rather cyclopentadiene formation by one of several alternative direct routes not involving (ground-state) I.

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The Sulfur Isotope Effect in the E2 Reaction of 2-Phenylethyldimethylsulfonium Bromide with Hydroxide Ion. A Correction[1]

Sir:

Some time ago, two of us[2] reported that the reaction of 2-phenylethyldimethylsulfonium bromide with hydroxide ion in water at 59° occurred with a very small sulfur isotope effect, the S^{32} compound reacting only 0.15% faster than the S^{34} compound. We recently had occasion to repeat this work, and we are now convinced that the original result is wrong.

The reactions were carried out essentially as before.[2] Table I gives the new results. In the experiments at Zagreb (series 1 and 2), the methyl sulfide was flushed from the reaction mixture by pure oxygen and the gas mixture was passed through a furnace at 1000° to obtain sulfur as sulfur dioxide, which was examined in a mass spectrometer. Series 2 utilized the same samples as series 1 after removal of all but 5% of the carbon dioxide produced in the combustion.[3] There is no significant difference except for the improved precision in series 2.

Table I. Sulfur Isotope Effects in the Reaction of 2-Phenylethyldimethylsulfonium Bromide with Hydroxide Ion in Water at 59°

Series	$((k_{32}/k_{34}) - 1)100^a$	
1^b	0.85, 0.60, 0.60, 0.64, 0.56	Av 0.65 ± 0.052^d
2^c	0.61, 0.60, 0.62, 0.58, 0.67	Av 0.62 ± 0.015^d
3^e	0.68, 0.65, 0.70, 0.64, 0.65, 0.61, 0.71	Av 0.66 ± 0.015^d
4^e	$0.63,^f$ $0.62,^g$ 0.61^h 0.58^i	Av 0.61 ± 0.11^d

[a] Except where otherwise noted, k_{32}/k_{34} is the ratio of S^{32}/S^{34} at 3% reaction (20 min) to S^{32}/S^{34} at 100% reaction (150–180 min). [b] Methyl sulfide combusted to $SO_2 + CO_2$. Samples contained *ca.* 70% CO_2. [c] Same as *b*, but samples contained <5% CO_2 (see ref 3 for method of removal). [d] Standard deviation of mean. [e] Isotope ratio measured directly on methyl sulfide from mass 62/mass 64. [f,g,h,i] S^{32}/S^{34} ratios determined at 10, 15, 20 and 30% reaction, respectively, and the isotope effect calculated from the formula of Stevens and Attree (ref 4).

In the experiments at Rochester, the only departure from the original procedure was to quench the reaction at the desired percentage completion by acidification with hydrochloric acid rather than by cooling. The methyl sulfide was expelled by nitrogen and purified, and the isotope ratio was determined as before. Series 3 utilized samples collected up to 3% reaction, but four runs from 10 to 30% reaction (series 4) were also done, and the isotope effect was calculated from the formula of Stevens and Attree.[4] The average of all of the results of series 3 and 4 is 0.64%, with a standard deviation of the mean of 0.012.

The excellent agreement of the values obtained by two different groups using two different methods is a gratifying demonstration of the precision with which isotope effects can be determined and makes it virtually certain that the original value[2] is erroneous. The two most probable reasons for the error are incomplete formation or collection of methyl sulfide in the "100%" runs and/or trace impurities in the reactants which could affect more strongly the samples taken at low completion. We favor the first explanation, for we noted no significant trend in the figures in series 4 as the extent of reaction increased.

The new value of the sulfur isotope effect makes it evident that the carbanion character in the transition state for the sulfonium salt is less extreme than formerly believed, for the effect is now *ca.* 30–40% of the experimental[2] and theoretical[5] maximum values.

A formerly puzzling situation is now cleared up. A comparison of the Hammett ρ values for the 2-phenylethyldimethylsulfonium and -trimethylammonium salts (+2.6[6] and +3.8,[7] respectively, at 30° in ethanol) indicates a transition state with higher carbanion character for the latter. In contrast to these facts was the nitrogen (N^{14}/N^{15}) isotope effect of about 1%[8] for reaction of the ammonium salt, a value which is much larger relative to the theoretical maximum[5] than was the old figure of 0.15% for the sulfonium salt relative to its theoretical maximum. The sulfonium salt is now seen to have a transition state with an extent of bond weakening to the leaving group at least as large as that for the ammonium salt, and the greater carbanion character with the ammonium salt is largely the result of more complete proton transfer to base.[9]

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